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Tuning structural dimensionalities of two new luminescent Cd(II) compounds: Different dicarboxylate coligands

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ABSTRACT

Two new Cd(II) compounds, namely $[Cd(tdc)(HPPA)]_n \cdot n(H_2O)$ (**1**) and $[Cd_3(obb)_2(PPA)_2(H_2O)_3]_n$ (**2**) (H_2tdc = 2,5-thiophenedicarboxylic acid, HPPA = pipemidic acid, H_2oba = 4,4′-oxybis (benzoate)), have been synthesized by incorporating pipemidic acid with Cd(II) ions and dicarboxylate coligands. Structural analyses reveal that compound **1** is a 1D chain structure, and further extended into a 2D supramolecular layered framework *via* intermolecular π…π and hydrogen bonding interactions, and compound **2** features a 3-fold interpenetrated 3D framework with 4-connected dia topology. HPPA ligand displays two different coordination modes in these two compounds. In addition, the thermal stabilities and luminescent properties of compounds **1** and **2** were also investigated in the solid state at room temperature.

1. Introduction

In the past few decades, coordination polymers (CPs) have experienced explosive growth, which have been proven to possess huge potential applications in the fields of catalysis, luminescence, magnetism, nonlinear optics, gas storage and so on [1–5]. However, controlling the structure and properties of the CPs still remains a great challenge owing to some unpredictable factors, such as temperature, pH value, solvent, metal ions, organic ligand etc [6–8]. Of all these factors, the selection of organic ligands is very important for the construction of CPs with desired structures and properties. Bi-functional organic ligands such as pyridine carboxylate, imidazol carboxylate, pyrazole carboxylate etc. have two different coordination sites (N-site and O-site), which can make them display variety of coordination modes. This structural characteristic makes them become very popular organic ligands for the synthesis of CPs [9–12]. Pipemidic acid (HPPA) simultaneously has two different potential coordination sites (N-site and O-site). Based on searching from the CCDC database, we found that pipemidic acid (HPPA) has been widely used for the construction of CPs [13–17], in which the HPPA ligands display two different coordination modes: monodentate mode and bidentate mode. In order to further enrich the coordination chemistry of HPPA ligand, in this work, we selected HPPA as the main organic ligand to construct functional CPs. In addition, we also select two different dicarboxylate ligands as the auxiliary coligand. Through the hydrothermal reaction of HPPA, auxiliary dicarboxylate ligand and Cd(II) ions, we successfully obtained two new CPs, namely $[Cd(tdc)(HPPA)]_n \cdot n(H_2O)$ (**1**) and $[Cd_3(obb)_2(PPA)_2(H_2O)_3]_n$ (**2**) (H_2tdc = 2,5-thiophenedicarboxylic acid, HPPA = pipemidic acid, H_2obb = 4,4′-oxybis (benzoate)). Compound **1** features a 1D chain structure and compound **2** features a 3-fold interpenetrated dia-type framework. *Via* altering the second coligand, we successfully realize the change of structural dimensionalities: from 1D to 3D.

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents employed in this work were commercially available and used without further purification. Elemental analyses (C, H and N) were determined with an elemental Vario EL III analyzer. Infrared spectrum using the KBr pellet was measured on a Nicolet Magna 750 FT-IR spectrometer in the range of 400–4000 cm^{-1}. Powder X-ray diffraction (PXRD) analyses were recorded on a PANalytical X'Pert Pro powder diffractometer with Cu/Kα radiation (λ = 1.54056 Å) with a step size of 0.05°. Thermal analyses were carried out on a NETSCHZ

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STA–449C thermoanalyzer with a heating rate of 10 °C/min under nitrogen atmosphere. Fluorescence spectra of the solid samples were performed on an Edinburgh Analytical instrument FLS920.

2.2. Synthesis of $[Cd(tdc)(HPPA)]_n \cdot n(H_2O)$ (**1**)

A mixture of $Cd(NO_3)_2 \cdot 6H_2O$ (0.058 g, 0.10 mmol), H_2tdc (0.017 g, 0.10 mmol), HPPA (0.03 g, 0.1 mmol), DMF(2 mL) and H_2O (2 mL) was placed in a small 20 mL glass vial. The resulting mixture was stirred for 30 min at room temperature, and then the mixture was kept at 110 °C for three days. After being slowly cooled to the room temperature, colorless block crystals of **1** were obtained in 42% yield based on $Cd(NO_3)_2 \cdot 4H_2O$. Anal. calc. for $C_{20}H_{21}N_5O_8SCd$ (603.89): C, 39.74; N, 11.59; H, 3.48%. Found: C, 39.68; N, 11.65; H, 3.52%. IR data (KBr pellet): 3450(s), 3179(m), 1652(m), 1626(m), 1550(s), 1478(s), 1431(m), 1182(s), 1135(m), 1034(m), 826(w), 807(m), 787(w), 610(m), 550(m), 519(m), 486(w).

2.3. Synthesis of $[Cd_3(obb)_2(PPA)_2(H_2O)_3]_n$ (**2**)

The synthesis of compound **2** was similar to that of **1**, but with H_2obb (0.036 g, 0.1 mmol) in place of H_2tdc. Colorless block crystals of **2** were obtained in 38% yield based on $Cd(NO_3)_2 \cdot 4H_2O$. Elemental analyses calcd. for $C_{56}H_{48}N_{10}O_{19}Cd_3$ (1502.27): C, 44.73; H, 3.20; N, 9.32%. Found: C, 44.78; H, 3.16; N, 9.36%. IR data (KBr pellet): 3450(s), 3179(m), 1652(m), 1626(m), 1550(s), 1478(s), 1431(m), 1182(s), 1135(m), 1034(m), 826(w), 807(m), 787(w), 610(m), 550(m), 519(m), 486(w).

2.4. X-ray crystallography

Suitable single crystals of **1** and **2** were carefully selected under an optical microscope and glued to thin glass fibers. Structural measurements were performed with a computer–controlled Oxford Xcalibur E diffractometer with graphite–monochromated Mo–Kα radiation (λ = 0.71073 Å) at T = 293 (2) K. Absorption corrections were made using the SADABS program [18]. The structures were solved by direct methods and refined by full–matrix least–square methods on F^2 by using the SHELXL–97 program package [19]. All non–hydrogen atoms were refined anisotropically. The H atoms attached to their parent atoms of organic ligands were geometrically placed and refined using a riding model. Crystal data, as well as details of data collection and refinements of **1** and **2** are summarized in Table 1, selected bond lengths and angles are given in Table 2.

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

Compound 1			
Cd (1)–O (4)[a]	2.169 (3)	Cd (1)–O (6)	2.253 (3)
Cd (1)–O (5)	2.262 (3)	Cd (1)–O (1)	2.362 (3)
Cd (1)–O (2)[b]	2.371 (2)	Cd (1)–O (2)	2.399 (2)
O (4)[a]–Cd (1)–O (6)	98.82 (11)	O (4)[a]–Cd (1)–O (5)	98.46 (11)
O (6)–Cd (1)–O (5)	77.62 (9)	O (4)[a]–Cd (1)–O (1)	113.98 (11)
O (6)–Cd (1)–O (1)	88.12 (9)	O (5)–Cd (1)–O (1)	146.27 (10)
O (4)[a]–Cd (1)–O (2)[b]	89.77 (10)	O (6)–Cd (1)–O (2)[b]	158.07 (9)
O (5)–Cd (1)–O (2)[b]	81.19 (9)	O (1)–Cd (1)–O (2)[b]	106.85 (9)
O (4)[a]–Cd (1)–O (2)	157.57 (11)	O (6)–Cd (1)–O (2)	100.22 (9)
O (5)–Cd (1)–O (2)	97.11 (9)	O (1)–Cd (1)–O (2)	55.19 (8)
Compound 2			
Cd (1)–N (3)[c]	2.319 (3)	Cd (1)–N (3)#2	2.319 (3)
Cd (1)–O (2W)	2.344 (3)	Cd (1)–O (8)[b]	2.449 (2)
Cd (1)–O (8)	2.449 (2)	Cd (1)–O (7)[b]	2.4666 (19)
Cd (1)–O (7)	2.4666 (19)	Cd (2)–O (6)	2.212 (2)
Cd (2)–O (7)	2.310 (2)	Cd (2)–O (1W)	2.326 (2)
Cd (2)–O (5)[a]	2.327 (2)	Cd (2)–O (1)	2.405 (3)
Cd (2)–O (2)	2.407 (3)	Cd (2)–O (4)[a]	2.531 (2)
N (3)[c]–Cd (1)–N (3)[d]	177.91 (13)	N (3)[c]–Cd (1)–O (2W)	88.96 (6)
N (3)[d]–Cd (1)–O (2W)	88.96 (6)	N (3)[c]–Cd (1)–O (8)[b]	90.79 (9)
N (3)[d]–Cd (1)–O (8)[b]	90.63 (9)	O (2W)–Cd (1)–O (8)[b]	132.88 (5)
N (3)[c]–Cd (1)–O (8)	90.63 (9)	N (3)[d]–Cd (1)–O (8)	90.79 (9)
O (2W)–Cd (1)–O (8)	132.88 (5)	O (8)[b]–Cd (1)–O (8)	94.23 (10)
N (3)[c]–Cd (1)–O (7)[b]	88.61 (8)	N (3)[d]–Cd (1)–O (7)[b]	91.04 (8)
O (2W)–Cd (1)–O (7)[b]	80.19 (5)	O (8)[b]–Cd (1)–O (7)[b]	52.70 (7)
O (8)–Cd (1)–O (7)[b]	146.90 (7)	N (3)[c]–Cd (1)–O (7)	91.04 (8)
N (3)[d]–Cd (1)–O (7)	88.61 (8)	O (2W)–Cd (1)–O (7)	80.19 (5)
O (8)[b]–Cd (1)–O (7)	146.90 (7)	O (8)–Cd (1)–O (7)	52.70 (7)
O (7)[b]–Cd (1)–O (7)	160.39 (10)	O (6)–Cd (2)–O (7)	78.88 (7)
O (6)–Cd (2)–O (1W)	83.79 (8)	O (7)–Cd (2)–O (1W)	159.66 (8)
O (6)–Cd (2)–O (5)[a]	139.81 (9)	O (7)–Cd (2)–O (5)[a]	93.68 (7)
O (1W)–Cd (2)–O (5)[a]	92.71 (8)	O (6)–Cd (2)–O (1)	92.98 (10)
O (7)–Cd (2)–O (1)	78.32 (10)	O (1W)–Cd (2)–O (1)	113.40 (11)
O (5)[a]–Cd (2)–O (1)	124.44 (9)	O (6)–Cd (2)–O (2)	136.23 (10)
O (7)–Cd (2)–O (2)	113.28 (9)	O (1W)–Cd (2)–O (2)	86.65 (9)
O (5)[a]–Cd (2)–O (2)	83.13 (9)	O (1)–Cd (2)–O (2)	52.73 (10)
O (6)–Cd (2)–O (4)[a]	86.96 (9)	O (7)–Cd (2)–O (4)[a]	89.54 (8)
O (1W)–Cd (2)–O (4)[a]	78.92 (9)	O (5)[a]–Cd (2)–O (4)[a]	53.26 (7)
O (1)–Cd (2)–O (4)[a]	167.61 (11)	O (2)–Cd (2)–O (4)[a]	132.64 (9)

Symmetry codes: compound **1** (a) $-1+x, y, z$; (b) $-2-x, 1-y, 1-z$. compound **2** (a) $1+x, -y, 0.5+z$; (b) $-x, y, 1.5-z$; (c) $-0.5+x, 0.5-y, 0.5+z$; (d) $0.5-x, 0.5-y, 1-z$.

Table 1
Crystal data and structure refinements for compounds **1** and **2**.

	1	2
Formula	$C_{20}H_{21}N_5O_8SCd$	$C_{56}H_{48}N_{10}O_{19}Cd_3$
Fw (g/mol)	603.89	1502.27
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*C*2/*c*
a (Å)	10.1960 (7)	14.9458 (5)
b (Å)	10.4168 (6)	26.4662 (8)
c (Å)	11.8391 (7)	15.3728 (5)
α(°)	102.958 (5)	90.00
β(°)	111.610 (6)	110.010 (4)
γ(°)	100.533 (5)	90.00
Volume (Å^3)	1089.31 (12)	5713.8 (3)
Z	2	4
Density (cm^3/g)	1.841	1.746
Abs. coeff. (mm^{-1})	1.159	1.192
Total reflections	7030	10906
Unique reflections	3771 (*R*int = 0.0308)	5038 (*R*int = 0.0201)
Goodness of fit on F^2	1.027	1.067
Final *R* indices [$I > 2$sigma (I^2)]	$R = 0.0335$, w$R_2 = 0.0743$	$R = 0.0289$, w$R_2 = 0.0740$
R (all data)	$R = 0.0413$, w$R_2 = 0.0792$	$R = 0.0413$, w$R_2 = 0.0792$